THE STRUCTURAL CHANGES OF WATER ICE I DURING WARMUP.

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ABSTRACT. We have mapped the polymorph transitions of vapor deposited water ice I during warmup from 15 K to 210 K by means of Selected Area Electron Diffraction. The polymorph transitions account for many phenomena observed in laboratory analog studies of cometary outgassing and radical diffusion in UV photolysed interstellar ices.

Vapor-deposited water ice, and mixtures containing water ice, are often studied in laboratory experiments in the context of the production of solid organic matter in interstellar space and the outgassing properties of comets. These experiments usually monitor gas release [1,2], infrared absorption bands [3,4], or heat release [5,6] during gradual warmup of ice layers. Although they address structural changes of the ice, all these methods are indirect. We have used Selected Area Electron Diffraction (SAED) in an instrumental configuration that allows dynamic observations of the ice structure during warmup and have mapped the polymorph transitions of water I [7].

Our results show distinct changes in the electron diffraction patterns due to a series of polymorph transitions [8]. Below 30K the vapor deposited ice is in a high density amorphous polymorph (I_ah). A sluggish transition to a low density amorphous polymorph (I_al) occurs between 45 K and 65 K (vapor deposition at 15 K at a rate of 18 micron/hr and subsequent warmup at 1-3 K/min). We have obtained the first structural evidence for a third amorphous polymorph of water with an on-set at 131-142 K (depending on annealing time). We refer to this polymorph as I_ac. I_ac persists when the ice crystallizes to a cubic I_c phase at 142-161K and only crystallizes into a hexagonal I_h crystalline phase at a temperature of about 225 K [9,10].

In dense interstellar clouds water mantles on dust grains are photolysed and recombination of the photolysis products results in small refractory molecules that are further processed by UV photons and cosmic rays into a poorly ordered hydrogenated amorphous carbon [11]. By comparing the transition regions found from our diffraction studies with studies reported in the literature, we find that radical diffusion and recombination occurs in the amorphous to amorphous transitions [8]. This probably accounts for the relatively high efficiency of residue formation in laboratory studies [11] and suggests that organic residue can form under astrophysical conditions in which temperature fluctuations below the sublimation limit occur together with amorphitisation by UV photons and electrons. This may also have implications for organic molecules that are thought to be formed on icy surfaces of some of the outer planets and their satellites.

Comets are thought to be the most primitive objects in the solar system, possibly containing pristine interstellar matter [12]. For both the study of planet formation and the study of comet formation and evolution, it is important to determine at what temperatures the cometary ice releases impurities and ulitmately volatilizes. By comparing the transition regions found above with the outgrassing studies reported in the literature [1,2], we find that it is mostly the amorphous to crystalline transition that accounts for outgassing [8]. Small volumes of gas release can, however, be associated with the amorphous to amorphous transitions.

These results apply to water dominated ices. However, cometary ices, for example, have been shown to contain 3-5 % methanol [13]. Seven percent methanol in a water ice matrix is enough to produce Type II clathrates above 130 K. In this case, clathrate formation is relevant to cometary outgassing phenomena [14].

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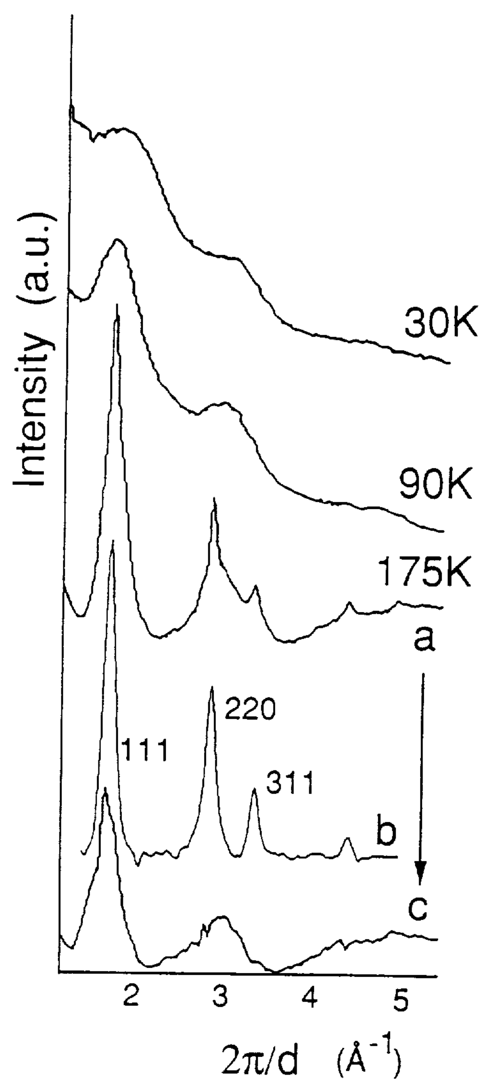

FIGURE. Examples of typical diffraction patterns obtained with Selected Area Electron Diffraction. The pattern taken at T=30 K is of polymorph I_ah, the one at T= 90 K is I_al, and the one at T=175 K contains both crystalline diffraction lines (b) of cubic I_c and an amorphous component (c) to which we refer as I_ac.